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Solution extraction of transition and post-transition heavy and precious metals by chelate and macrocyclic ligands

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Contents

Abstract

This review focuses on compounds and methods that can be used for the extraction and separation from solution of two classes of elements that we define as heavy metals and precious metals. These elements are often targeted because they are toxic, costly, and their coordination chemistry has already been well studied, and because there is a need to develop methods of economically extracting, separating and recovering them from waste sites. This review outlines possible strategies that can be used, and reviews the present literature regarding the available methods for their extraction. © 1998 Elsevier Science S.A.

Keywords: Extraction; Separation; Heavy metals; Precious metals

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1. Heavy metals

In order for a metal to be given high priority for removal it should meet the following criteria. One is that the metal should be present in quantities that pose a serious health threat to humans. A second is that the targeted metal has sufficient commercial value that its resale can recover the costs of the extraction process. When both criteria are met there is a strong impetus to develop extractants that are selective for the individual metals.

A broadly defined group of elements classified as heavy metals contain a number of members that are toxic either by virtue of their interaction with enzymes, their tendency to bond strongly with sulfhydryl (–SH) groups on proteins, or other in vivo effects [1]. Some of these elements are transition and post-transition metals (cadmium, mercury, copper, zinc, chromium), while others are main group elements (barium, thallium, lead). Inorganic forms of most heavy metals form strong bonds with proteins and other biological tissue, thus increasing bioaccumulation and inhibiting excretion. Tissues often exhibit a significant selectivity when binding to these metals. Lead, for example, tends to accumulate in bone tissue, while cadmium and mercury predominantly accumulate in the kidneys. The donor groups that are most available for in vivo binding to metal ions are amino and carboxyl groups. Binding is especially strong for many heavy metals to thiol (sulfhydryl) or thiolate groups. This feature is particularly significant because –SH groups are a common component of the active sites of many important enzymes, including those involved in energy output and oxygen transport. Because of the combination of a widespread possibility for human exposure coupled with an extremely high toxicity, certain heavy metals are a particular concern with regard to their toxic effects. These metals are chromium, cadmium, mercury and lead.

As a result of decades of industrial production involving their use, heavy metal contamination of soils and aquifers is becoming increasingly common at many hazardous waste sites. Solid wastes generated through the mining and processing of mineral ores also often contain residual metals along with other substances [2]. Improperly disposed mineral waste piles can be subject to severe wind and water erosion, resulting in transport of the contaminated material inherent in the wastes. Moreover, leakage generated from waste piles can pollute nearby groundwater systems and surface streams, rendering valuable water supply sources unsuitable for use. Other activities contributing to heavy metal contamination of soil and aquifers include vehicle emission, smelting, metal plating and finishing, battery production recycling, agricultural and industrial chemical application, and incineration processes. Once released into the soil matrix these metals are strongly retained by the anionic zeolites present. Thus their adverse impact on environmental quality and on human health often persists for substantial periods of time. As a result, studies focused on metal ion removal from both aqueous solutions and soils, either for pollution control or for raw material separation and recovery, have become of increasing importance in recent years. This is particularly true for metals that have both high toxicity and a high commercial value if they can be recovered in pure form.

2. Precious metals

Another area where a strong demand for new methods of metal extraction and separation exists in the commercial sector is in the recovery and separation of precious metals. Precious metals such as silver, gold, palladium and platinum possess similar chemical properties and are of commercial importance in the catalyst, jewelry and electronics industries. Many traditional processes for the extraction and purification of precious metals from their ores are pyrometallurgical [3]. These methods are most suited to the treatment of high-grade ores and concentrates. With the depletion of many high-grade ores, methods for effecting ore concentration have become increasingly important, and there is increased demand to process low-grade materials. There has accordingly been developments in the treatment of ores by both hydrometallurgical and solvent extraction processes. These processes employ aqueous or organic media at essentially ambient temperatures, so they are cost effective and relatively non-polluting when compared with pyrometallurgical extraction methods.

In the analytical field the determination of trace amounts of heavy and precious metals in various materials often requires their preliminary concentration and separation from large amounts of other metals. An emerging area for the application of highly selective metal ion extracting agents is therefore in the preconcentration of specific metals.

3. Strategies for obtaining metal ion recognition

The most commonly used treatment methods for heavy metal-containing waste presently include precipitation, solvent extraction, activated carbon adsorption, treatment with ion exchange resins and bioremediation. Other methods that are less widely used include reverse osmosis, electrolysis, cementation, irradiation, zeolite adsorption, evaporation, membrane processes and ion flotation [4].

Solvent extraction occurs when a metal ion associates with an organic complexant to form a species that is transferred from the aqueous to the organic phase in a two phase system. While most laboratory work has been carried out with chloroform as the organic phase, kerosine and hexane are preferable for industrial applications because of their lower toxicity. Carbon dioxide is also becoming frequently used for the solid–liquid extraction of heavy metals from contaminated soils.

Two types of liquid–liquid extractions that are frequently encountered are:

(1) when the complexants are both soluble in the aqueous phase, and the extracted metal species are soluble in the organic phase;

(2) when the complexants are insoluble in the aqueous phase, then the complexation occurs at the interphase surface, and the metal species are then transferred into the organic phase.

Two groups of organic compounds that have been widely used for metal extractions are chelate and macrocyclic ligands [5,6]. These are chosen because of the highly favored complexation due to the chelate and macrocyclic effects. The term "chelate effect" refers to the enhanced stability of a complex formed between a metal ion and a ligand that contains multidentate binding sites as compared to an analogous ligand that contains only a single binding site. The term "macrocyclic effect" refers to the greater thermodynamic stability of a complex that has a cyclic polydentate ligand as compared to the analogous complex that has an acyclic chelate ligand. The most efficient use of extracting agents requires that the following conditions are met:

(1) good ion uptake by the complexant thereby allowing fast binding,
(2) high stability against hydrolysis,
(3) selective ion complexation with no affinity for alkali or alkaline earth ions whose concentrations are usually high in natural waters and soils,
(4) sufficiently high binding strength for the metal ions to be extracted,
(5) reversible complexation allowing for total recovery of the metal without significant ligand or resin destruction [7].

From studies of the interaction of transition metals and other heavy metals with macrocyclic ligands three major strategies emerge for achieving effective complexation [8]:

(1) use of ring size variation to maximize the thermodynamic stability of the complex by matching the radius of the metal ion to the hole size of the macrocyclic ligand,
(2) use of donor set variation to alter the affinities of the ligand systems towards particular metal ions,
(3) use of substituent variation to take advantage of the effect of appended substituents to the donor atoms of the parent macrocycle on metal ion discrimination.

Arland [9] has proposed a classification according to which metal ions can be subdivided into three groups. These are elements that form the most stable complexes with the first element of their group in the periodic system, (N, O, F); elements that form the most stable complexes with atoms of the second or the lower elements of their group (P, S, Cl); and elements that display an intermediate behavior between these two options. It is also possible that different valence states of a particular metal may behave in a different manner.

4. Extraction of heavy and precious metals with chelate agents

A chelating agent by definition has at least two donor atoms that are coordinated to the same metal [10]. Such atoms are usually oxygen, nitrogen and sulfur, but selenium, tellurium and others may also be the donors. In designing extractants an additional advantage can be gained if the chelating agent has acidic hydrogens that can be substituted by metal ions during complex formation. Such a condition can lead to the formation of an uncharged complex. The complex to be extracted, even if uncharged, should be as hydrophobic as possible, especially if it is desired to employ a nonpolar solvent for the phase transfer extraction. One of the earliest reports of chelate extraction was that of Cazeneuve [11] who in 1900 described how chromium could be extracted by a benzene solution of 1,5-diphenylcarbohydrazide. Now there are many examples of organic chelates being employed as extractants for heavy and precious metal ions [3,7,12–45]. The following sections summarize the most commonly used chelate extractant agents and the heavy and precious metal ions for which they have been used. These chelate agents have been divided into four major groups depending on their structure and donor atom types.

4.1. *Dithio- and diselenocarbamates*

Dithiocarbamates, and especially their ammonium and sodium salts, are widely used as extractants for transferring heavy metal ions into an organic phase. In general, an excess of dithiocarbamate is added to the aqueous solution containing the metal ions to be extracted, and the complexed neutral species are then extracted into the organic phase. The data in Table 1 summarize the extraction properties of sodium diethyldithiocarbamate (Na–DDC) [12,46], zinc dibenzyldithiocarbamate (Zn–DBDTC) [13], hexamethyleneammonium hexamethylenedithiocarbamate (HMA–HMDC) [14,15,17], ammonium pyrrolidine dithiocarbamate (APDC) [19], diethylammonium diethyldithiocarbamate (DDDC) [19], ATMDTC [20], ethylene bis-dithiocarbamate, propylene bis-dithiocarbamate, butylene bis-dithiocarbamate, pentamethylene bis-dithiocarbamate and hexamethylene bis-dithiocarbamate (Fig. 1) [22]. Sodium dibutyldiselenocarbamate is the only selenocarbamate that has been widely used for the extraction of heavy metal ions [21]. Both dithio- and diselenocarbamates show a high pH dependent extractability but overall poor selectivity. These ligands form covalent species with most transition and heavy metals, with the latter being almost always extracted together into the organic phase. Nevertheless, despite this lack of selectivity, there are several methods available for using these ligands to concentrate heavy metals into an organic phase until they reach limits detectable by AAS and ICP-AES. For example, dithiocarbamate complexes of heavy metals have different retention times, and thus they can be used in the GC and HPLC determination of heavy metals present in aqueous solution [15,17,46]. A second example involves bis-(carboxylmethyl)dithiocarbamate (CMDTC) that has been pre-treated with $SnCl_2$ and HCl. This product can be incorporated onto the polystyrene–divinylbenzene resin (XAD-4), and the modified resin used for the preconcentration of Pd, Pt and Rh [47].

Long chain alkyl and choline substituted xanthates have also been used as extractants for Cd(II), although dithiocarbamates are generally preferred because of the ready loss of carbon disulfide from the xanthate ligand [48].

4.2. *Aminopolycarboxylic acids, amides and aminimides*

Aminopolycarboxylic acids are a class of water soluble chelating agents that are widely used for the extraction of heavy metal ions from soils and other solid phases into water or, when attached to polymeric support, for heavy metal removal from aqueous solution. Iminodiacetic acid, for example, when attached to a cellulose

Table 1
Summary of extractants and their selectivities

Compound number	Structural formula	Extracted species	References
1	Sodium diethyldithiocarbamate	Cd(II) in liver and kidney	[46]
2	Zinc dibenzylidithiocarbamate	Pb(II), Ag(I), Sb(III), Bi(III), Tl(I)	[13]
3	Hexamethyleneammonium hexamethylenedithiocarbamate (HMA–HMDC)	Ag(I), Bi(III), Cd(II), Cu(II), Pb(II), Tl(I), Zn(II), Hg(II)	[14,15,17]
4	Sodium diethyldithiocarbamate and ammonium pyrrolidinedithiocarbamate (APDC)	Hg(II), Bi(III), Cu(II), Pb(II), Cd(II), Cr(VI)	[12]
5	APDC and DDDC	Zn(II), Cu(II)	[19]
6	APDC	Cu(II), Pb(II), Cd(II)	[18]
7	Ammonium tetramethylene dithiocarbamate (ATMDTC)	Cd(II), Pb(II), Cu(II), Zn(II), Cr(III), Ba(II)	[20]
8	EBDTC, PBDTC, BBDTC, PMBTC, HMBDTC, Fig. 1	Cu(II), Zn(II), Cd(II), Pb(II), Cr(VI)	[22]
9	Sodium dibutyldiselenocarbamate	Au(III), Cu(II), Hg(II), Pd(II), Zn(II)	[21]
10	Bis(carboxymethyl)dithiocarbamate (CMDTC)	Pd(II), Pt(II), Rh(III)	[47]
11	Xanthates	Cd(II)	[48]
12	Cellulose–N$(CH_2CO_2H)_2$, Fig. 2	Cr(III), Cu(II), Pb(II)	[49]
13	ADA and SCMC, Fig. 3	Pb(II), Cu(II), Zn(II)	[23–25]
14	Na_2EDTA	Cd(II), Cr(III), Cu(II), Pb(II), Zn(II)	[50]
15	NTA, EDTA, EGTA, DTPA	Pb(II), Zn(II), Cu(II)	[26]
16	DTPA, EDTA	Zn(II), Cu(II), Cd(II), Pb(II), Cr(III)	[28]
17	Fig. 4	Zn(II), Pb(II), Cd(II), Cu(II)	[29]
18	Fig. 5	Cu(II), Zn(II), Cr(III)	[55]
19	Fig. 6	Cu(II)	[39]
20	Fig. 7	Pd(II), Pt(II), Ru(III), Au(III), Rh(III), Os(III), Ir(III), Cu(II), Hg(II), Pb(II), Zn(II), Cd(II)	[40]
21	Fig. 8	Cu(II), Ag(I), Pb(II)	[35]
22	Fig. 9	Cu(II)	[51]
23	Fig. 10	Cu(II), Bi(III), Cr(III), Pb(II), Zn(II)	[58]
24	Fig. 11	Pd(II), Cu(II), Pt(II), Rh(III)	[59]
25	Fig. 12	Pd(II)	[36]
26	Fig. 13	Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Bi(III), Au(III)	[32]
27	5,7-Dichloro-8-quinolol	Cd(II), Pb(II), Zn(II), Cu(II)	[60]
28	Fig. 14	Cu(II), Zn(II), Cd(II)	[31]
29	Fig. 15	Co(II)	[33]
30	Fig. 16	Ag(I), Cd(II), Cu(II), Pb(II)	[34]
31	Alkyl-8-hydroxyquinolines	Cu(II), Ni(II), Zn(II), Cd(II), Hg(II)	[61,62]

Table 1 (*continued*)

Compound number	Structural formula	Extracted species	References
32	Fig. 17	Cu(II), Fe(III)	[63]
33	Fig. 18	Pb(II), Cu(II)	[41]
34	Fig. 19	Zn(II), Cu(I)	[37]
35	Fig. 20	Ag(I), Pb(II)	[64]
36	Fig. 21	Pd(II), Ag(I)	[45]
37	Fig. 22	Pb(II), Hg(II), As(III) in CO_2	[65]
38	Fig. 23	Pb(II), Cd(II), Zn(II), Cu(II)	[30]
39	Bis(phenoxyalkyl)sulfanes	Ag(I)	[66]
40	Fig. 24	Ni(II), Pd(II), Pt(II), Bi(III)	[69]
41	PAQH	Ni(II), Cu(II), Zn(II), Cd(II)	[70]
42	Fig. 26	Hg(II), Cu(II), Pb(II)	[7]
43	Fig. 27	Cu(II), Hg(II)	[74,75]
44	Fig. 28	Cu(II), Hg(II), Pb(II)	[77]
45	Fig. 29	Cu(II), Hg(II), Pb(II)	[78]
46	Fig. 30	Cu(II), Zn(II), Cd(II), Pb(II), Ag(I)	[76]
47	Fig. 31	Cu(II), Ag(I), Pb(II), Hg(II), Zn(II), Cd(II)	[85]
48	Fig. 32	Ag(I), Cu(II), Pb(II), Zn(II)	[84]
49	Fig. 33	Hg(II), Pb(II), Cu(II), Cd(II), Ba(II)	[88]
50	Fig. 34	Ag(I), Tl(I), Ba(II)	[80]
51	Fig. 35	Tl(I), Ag(I), Ba(II)	[81,82]
52	Fig. 36	Ag(I), Tl(I)	[83]
53	Fig. 37	Cu(I), Pd(II), Ag(I), MeHg(II), Hg(II)	[79]
54	Fig. 38	Cu(II), Zn(II), Cd(II), Pb(II)	[110]
55	Fig. 39	Pd(II), Au(III), Ag(I), Hg(II)	[111]
56	Fig. 40	Ag(I)	[87]
57	Fig. 41	Ag(I), Hg(II)	[112]
58	Fig. 42	Ag(I)	[86]
59	Triazine thiols	Tl(I), Ag(I), Hg(II)	[113]
60	Fig. 43	Ag(I), Au(III)	[115]
61	Fig. 44	Ag(I), Tl(I)	[117]
62	Fig. 45	Ag(I), Tl(I)	[91]
63	Fig. 46	Cu(II), Cd(II), Pb(II)	[90]
64	Fig. 47	Ag(I), Pb(II)	[118]
65	Fig. 48	Hg(II), Hg(I), MeHg(II), Cd(II), Pb(II), Pd(II), Ag(I), Au(III), Pt(II)	[119]
66	Fig. 49	Hg(II), Cu(II), Cd(II)	[123]
67	Fig. 50	CrO_4^{2-}	[124]

sorbent (Fig. 2), is used for the pH dependent removal of Cr(III), Cu(II), Pb(II) and Ni(II) from water [49]. Metal recovery from the material can be accomplished by elution with 3M nitric acid. The derivative *N*-2-acetamidoiminodiacetic acid (ADA) selectively extracts Zn(II) from spiked soils in the presence of Fe(III) and Ca(II) [24], and both ADA and *S*-carboxymethyl-L-cysteine (SCMC) (Fig. 3) are

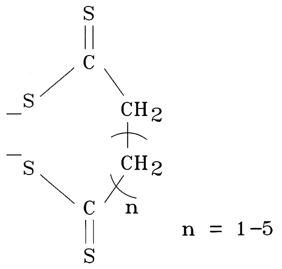


Fig. 1. Structure of bis-dithiocarbamates.

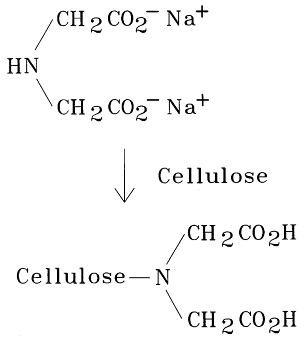
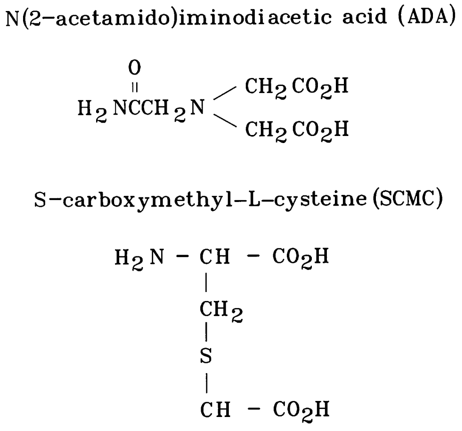


Fig. 2. Cellulose-bound iminodiacetic acid.


N(2-acetamido)iminodiacetic acid (ADA)

S-carboxymethyl-L-cysteine (SCMC)

Fig. 3. Structures of ADA and SCMC.

used for the extraction of both Pb(II) and Cu(II) from contaminated soil [23,25]. One of the best known chelates, the hexadentate ethylenediaminetetraacetic acid (EDTA) [50], has been used for the removal of Cd, Cr, Cu, Fe, Pb, Ni and Zn from sludge. The high toxicity of EDTA, however, precludes its more widespread use. The closely analogous compounds nitrilotriacetic acid (NTA) and ethyleneglycol bis(2-aminoethylether) tetraacetic acid (EGTA) [26] have been similarly used. Diethylenetriaminepentaacetic acid (DTPA) has been used for the extraction of Pb, Ni, Cu and Zn [28]. Another water soluble agent used for the modification of silica gel is Methylthymol Blue or the 3,3′-bis[*N*,*N*-di(carboxymethyl)aminomethyl]thymol sulfonephthalein sodium salt (Fig. 4) [29]. The modified material extracts a wide range of metals such as Ca, Mg, Al, Cu, Fe, Co, Ni, Zn, Cd, Pb, Cr and Bi.

Extractants can also be used to mobilize heavy metals from a soil matrix. Thus the concentration of soluble Ni, Pb and Zn increases in soil–sludge mixtures upon addition of the complexant nitrilotriacetic acid (NTA). A lesser effect is found for Cu, and only minimal effect is observed with this extractant for Mn [51]. The chelating extractant APDC has been used to preconcentrate Cd, Cu, Pb and Zn from seawater. Nitric acid can then be used to recover these metals back from the organic phase [52]. Sandy soils contaminated with Cd, Zn, Cu and Pb can be cleansed by sequential washing first with $Na_4P_2O_7$, then with the chelate extractant EDTA [53].

Commercial extractants have found application for heavy metal removal. A microporous hydrophobic hollow fiber membrane-based solvent extraction device, along with the chelate LIX84, can be used to extract Cu(II) [54]. Silica gel impregnated with a mixture of Aliquat 336 and Calcon (Fig. 5) can be used for the preconcentration of Mg, Ca, Cu, Zn, Al, Cr and Fe. The reagent is an effective extractant for even trace concentrations of these metals [55]. Silica impregnated with a mixture of Aliquat 336 and Titan Yellow can be used as an extractant for the metals Ca, Mg, Al, Cu, Fe, Ni, Co, Cd, Zn, Pb, Hg and Cr. Elution from the resin can be effected with a dilute solution of either HCl or $HClO_4$ [56].

Amides and aminimides bearing lipophilic groups are water insoluble complexants that are useful for the extraction of metal ions from water into an organic phase.

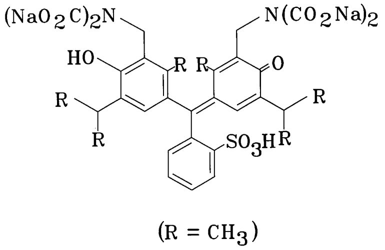


Fig. 4. Water soluble complexant for a series of metals.

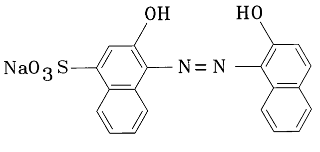


Fig. 5. Structure of Calcon.

Disubstituted pyridines (Fig. 6) selectively extract Cu(II) in the presence of Ni(II), Co(II) and Zn(II) [39]. *N*-Acylated ureas, thioureas and selenoureas (Fig. 7) extract almost all heavy and transition metal ions [40]. The aminimide shown in Fig. 8, however, selectively extracts Cu(II), Ni(II) and Ag(I) [35].

The azoles, pyrazole, imidazole, 1,2,4-triazole and tetrazole when immobilized onto either poly(glicidyl methacrylate) or its sulfur analog (Fig. 9) are highly selective extractants for Cu(II) in the presence of Ni(II), Co(II), Zn(II) and Cd(II). There is no metal ion uptake onto these modified resins below pH 2.5, and indeed the resins can be regenerated by the addition of 1M H_2SO_4 [57].

4.3. Oximes and hydroxyaromatic derivatives

Water soluble oximes and hydroxyaromatic derivatives form stable chelates with many metal ions that are extractable into organic solvents. The compound 1-(2-hydroxy-5-β-hydroxyethylsulfonyl-phenylazo)-2-naphthol (Hyphan I, Fig. 10) forms stable extractable 1:1 complexes with Cu(II) and U(VI) in weakly acidic solutions, while at pH>8 this complexant can be used to quantitatively extract

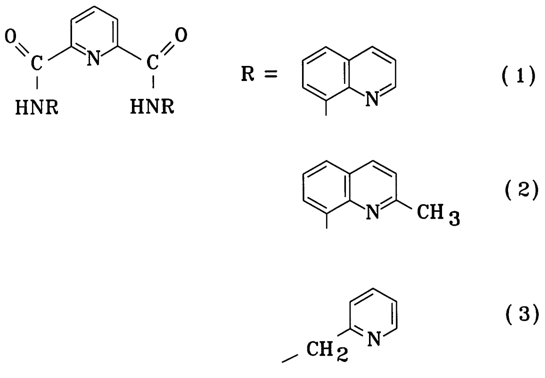


Fig. 6. Disubstituted pyridine extractants.

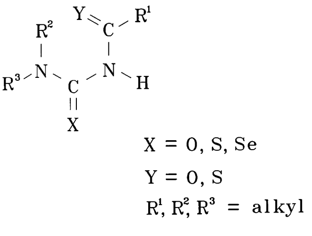


Fig. 7. Structures of substituted ureas.

$$C_6H_{13}CH(OH)CH_2C(O)\overset{-}{N}\overset{+}{N}(CH_3)_2CH_2CH(OH)C_6H_{13}$$

Fig. 8. Aminimide extractant.

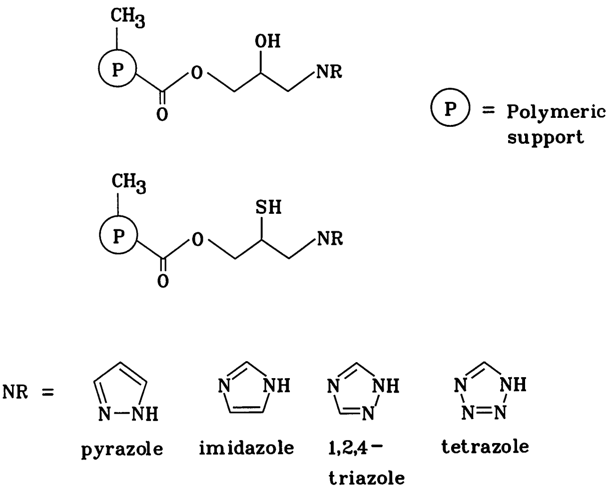
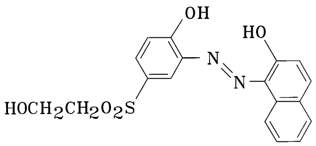


Fig. 9. Polymer-bound azoles.



Hyphan I

Fig. 10. Structure of hyphan I.

Be(II), Bi(III), Cr(III), Mn(II), Pb(II) and Zn(II) [58]. A similar derivative, 1-(2-pyridylazo)-2-naphthol (PAN, Fig. 11) can be used in conjunction with liquid chromatography for the separation of the platinum group metals Pd(II), Pt(II) and Rh(III) from Ni(II), Cu(II), Co(III) and other heavy metals [59]. The rapid separation of Pd(II) from other metals has been achieved by extraction with isonitrosoacetophenone (HINAP, Fig. 12) [36]. The complexants HINAP, 5,7-dichloro-8-quinolinol, and di-2-pyridyl ketone salicyloylhydrazone (DPKSH, Fig. 13) and its

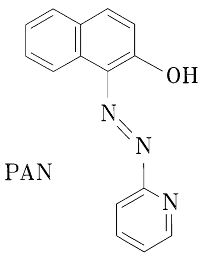
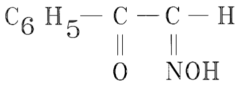


Fig. 11. Structure of PAN.

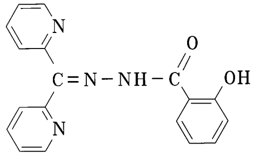


$C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-H$

HINAP

Fig. 12. Structure of HINAP.

DPKSH



DPKBH

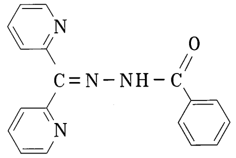


Fig. 13. Structures of DPKSH and DPKBH.

benzoylhydrazone (DPKBH) are used for the preconcentration and subsequent AAS or ICP-AES determination of traces of heavy metals [32,60]. The compound 5,7-dichloro-8-quinolinol has been used for Cd, Pb, Zn, Fe, Cu, Ni, Mo and V, and DPKSH and DPKBH have been used for Fe, Co, Ni, Cu and Zn. Other chelating agents from this group that have been used are 3-[(dioctylamino)methyl]alizarin (C8AL, Fig. 14) for Cu, Zn, Cd, Co, Mn, Ni and Fe [31], 2-nitroso-1-naphthol (2-nitroso-N, Fig. 15) and 1-nitroso-2-naphthol (1-nitroso-N, Fig. 15), [33] and 4-(2-pyridylazo)resorcinol (PAR, Fig. 16) [34].

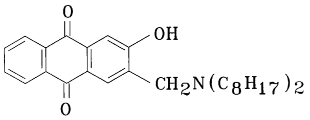
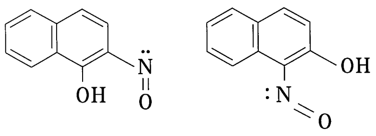
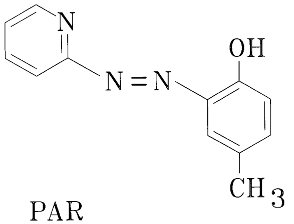


Fig. 14. Structure of C8AL.



2–nitroso–N 1–nitroso–N

Fig. 15. Structures of 2-nitroso-N and 1-nitroso-N.



PAR

Fig. 16. Structure of PAR.

Alkyl-8-hydroxyquinolines show high extractabilities for Cu(II), Ni(II), Zn(II), Cd(II) and Hg(II). The addition of decanol to the organic phase causes a significant increase in metal extraction because of the alcohol solvation of the extracted complex [61]. Of these complexants the 2-nonyl-8-hydroxyquinoline derivative (N,O) is the best extractant. Molecular modeling calculations support a hexacoordinate cadmium complex of the $Cd(NO)_2(decanol)_2^{2+}$ or $Cd(NO)_2(H_2O)(decanol)^{2+}$ type [62]. The complexant salicylic acid (Fig. 17) in the presence of triisoamyl phosphate (TAP) has been used for the extraction and separation of Cu(II) and Fe(III). This mixture has also been used for the partial extraction and separation of Cr(III), Mn(II), Ni(II), Zn(II), Pb(II) and Cd(II) [63].

4.4. Others

Other chelating agents that have been used for the extraction of heavy metal ions are lipophilic and oligomeric polyethers (Fig. 18) that exhibit high selectivity toward Pb(II) over Cu(II) [41]; polyethers (Fig. 19) that selectively extract Zn(II) and Cu(I) over Fe(III), Co(II), Ni(II), Mn(II) and Cr(III) [37]; and oxygen, nitrogen and sulfur donor sets contained in a series of chelating agents (Fig. 20) that exhibit high selectivity for Ag(I) over Pb(II) [64]. A series of thiophosphonyl derivatives (Fig. 21) efficiently extract Pd(II) and Ag(I) [45]. A group of fluorinated chelating agents (Fig. 22) that possess high solubilities in liquid carbon dioxide can be used for the supercritical extraction and recovery of Pb(II), Hg(II) and As(III) from soil matrices [65]. Other multidentate *N,O*-chelates that have been used for the extraction of Pb(II) over Cd(II), Zn(II) and Cu(II) are shown in Fig. 23 [30].

Bis(phenoxyalkyl) sulfane podands have been prepared that can be structurally modified to be selective extractants for Ag(I). The highest extractability is observed

Salicylic acid

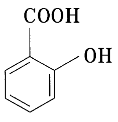


Fig. 17. Structure of salicylic acid.

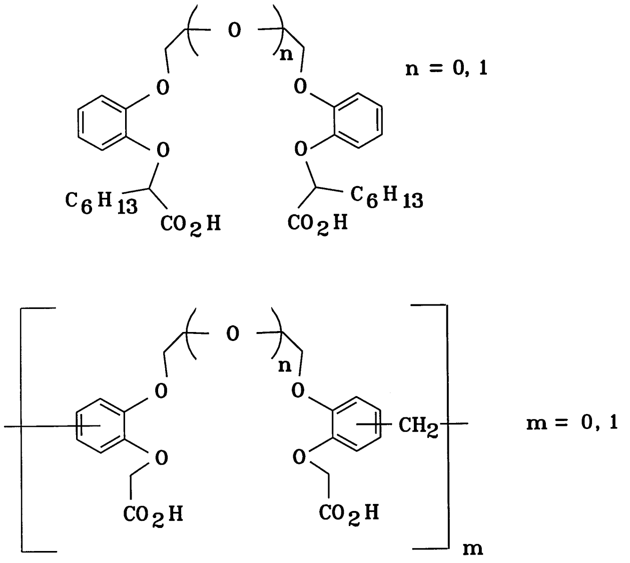


Fig. 18. Structures of lipophilic polyethers.

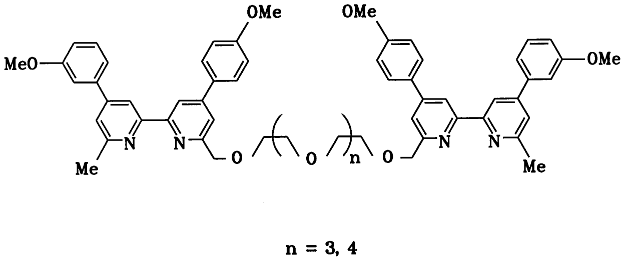


Fig. 19. Structure of bipyridyl capped polyethers.

with the bis[(5-hydroxy-3-oxapentyloxy)-3-phenoxy-prop-2-yl] sulfane [66]. Comparative extractabilities of Hg(II), Zn(II), Cd(II) and Cu(II) by Aliquat 336, di(2-ethylhexyl) phosphoric acid, acyl thiourea and oxathiaazaalkanes have been examined. The advantages and disadvantages of each system are discussed, with a conclusion being drawn that Aliquat 336 is effective for mercuric chloride solutions and for the extraction of cadmium and zinc from copper. Metal recovery is achieved using ethylenediamine [67]. A systematic study of the extraction of $HgCl_2$ by a series of thiaoxaazaalkanes has shown that the extractability decreases in the order NN > NS > NO > SS > SO. The highest extractability is observed where five-membered chelate ring formation can occur [68]. A series of 1,2-dithiolate ligands (Fig. 24) have been used as extractants for a broad range of transition metal ions [69]. Selectivity is quite low.

The compound pyridine-2-aldehyde-2-quinolylaldehyde (PAQH) (Fig. 25) is an effective extractant for transferring Ni(II), Cu(II), Co(III), Fe(II), Zn(II) and

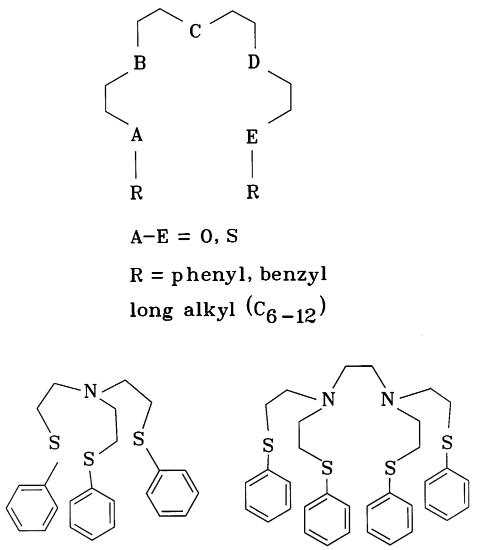
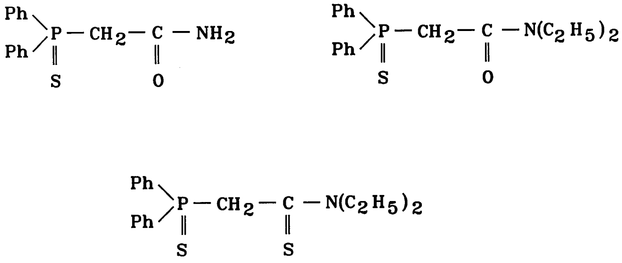


Fig. 20. Structures of O, S and N, S chelates.

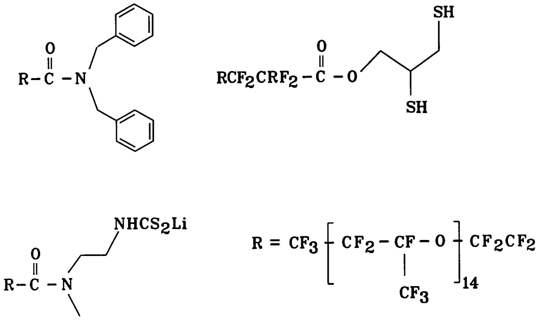


$Ph_2P(=S)-CH_2-C(=O)-NH_2$

$Ph_2P(=S)-CH_2-C(=O)-N(C_2H_5)_2$

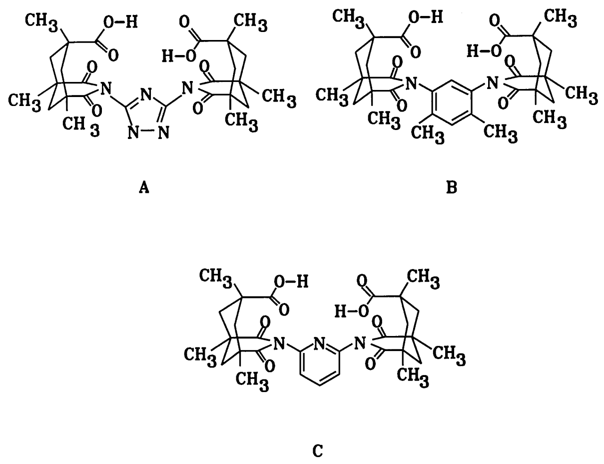
$Ph_2P(=S)-CH_2-C(=S)-N(C_2H_5)_2$

Fig. 21. Structures of thiophosphonyl complexants.



$$R = CF_3\left[CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-O\right]_{14}CF_2CF_2$$

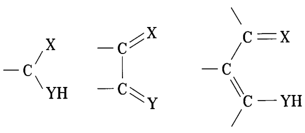
Fig. 22. Structures of fluorinated complexants.



A B

C

Fig. 23. Structures of multidentate N, O chelates.



X, Y = 0, S, Se

Fig. 24. Generalized forms of O, S, Se chelates.

PAQH
(pyridine-2-aldehyde-2-quinolyl-hydrazone)

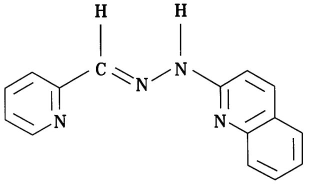


Fig. 25. Structure of PAQH.

Cd(II) into benzene, isoamyl alcohol and methyl isobutyl ketone [70]. A 30% *N,N*-methylenebis(acrylamide) cross-linked poly[*N*-((acryloylamino)methyl)mercaptoacetamide] resin (Fig. 26) has been used for the extration of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Hg(II), Pb(II) and UO_2(VI). The resin activity at pH 5.5 follows the metal ion sequence Zn(II) < Cd(II) < Pb(II) < Cu(II) < Hg(II) [7].

Supercritical carbon dioxide, along with chelates that are soluble in liquid carbon dioxide, have been used for the extraction of mercury, arsenic and lead from soils

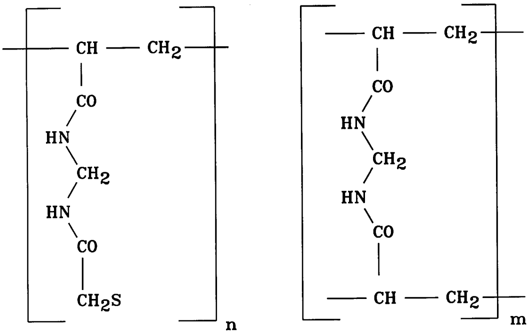


Fig. 26. Structures of derivatized resins.

[71]. Chelate solubility in carbon dioxide has been achieved by the incorporation of long fluorinated or silicone-based tails. Krytox ($CF_3[CF_2CF(CF_3)O]_{14}CF_2CF_2$–) has been used as the fluorinated tail, and the functionality –$O(CH_2)_3[SiO]_3Si(CH_2)_3Si[OSi(CH_3)_3]_3$ as the silicone tail. The compound 3-(2-aminoethylamino)propyltrimethoxysilane (Dow Corning Z-6020) has been attached to silica gel. This reagent, which structurally has a substituted ethylenediamine moiety present, can be used to extract Cu(II), Zn(II), Cr(III), Mn(II), Pb(II) and Hg(II) [72]. Synergistic extraction of Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) with dithizone and tributylphosphine oxide has also been achieved. The pH limit for each metal ion has been calculated [73].

5. Extraction of heavy and precious metals with macrocyclic agents

Recently there has been a considerable amount of work carried out on the interaction of heavy and precious metals with macrocyclic compounds, including crown and lariat ethers, cryptands and calixarenes [74–93]. Within this work there have been many studies of macrocycles binding with transition metal ions in a single solvent [94,95]. Nevertheless, only a few extraction studies of transition metals salts with macrocyclic ligands have been reported [95,96]. In general oxygen macrocycles such as crown ethers are effective for the extraction of alkali and alkaline earth metal salts, but not for transition metal salts. By contrast, the nitrogen analogue macrocycles are effective for transition metal salts but not for alkali metal salts [97–109]. The following section summarizes the available macrocyclic extractant agents and the metal ions that they extract.

5.1. *Crowns and thiacrowns*

One of the earliest literature reports concerning the use of a macrocyclic agent for the extraction of heavy and precious metals is that of Shinkai *et al.* [74,75] who synthesized a photoizomerizable azobenzene-bridged crown ether (Fig. 27) that

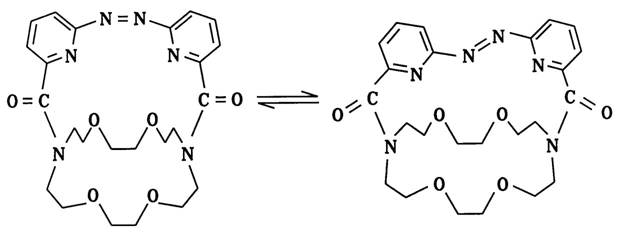
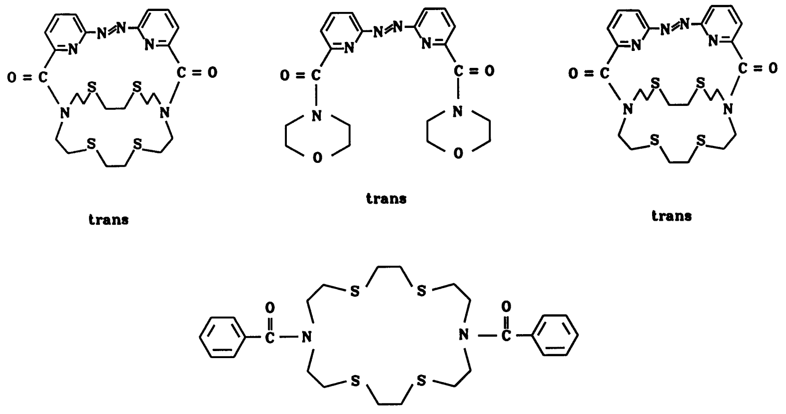


Fig. 27. Structures of isomeric forms of the photoisomerizable azobenzene-bridged crown ether.

extracts Pb(II) and to a lesser extent, other metal ions. The *trans* isomer extracts metal ions to a much greater extent than does the *cis* isomer. This was the first example of a photoresponsive cryptand for the solution extraction of heavy metal cations. Subsequently this research group has reported a new photoresponsive cryptand based on a thiacrown ether [77]. Both the *trans* and *cis* isomers of these complexants (Fig. 28) are good extractants of Cu(II) and Hg(II) in the presence of Co(II), Ni(II) and Pb(II). A similar set of photoresponsive thiacrown ethers (Fig. 29) nonselectively extract Cu(II), Hg(II), Co(II), Ni(II) and Pb(II) [78]. The liquid–liquid extraction of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II) and Ag(I) with the tetraazamacrocycles shown in Fig. 30 has been reported [76]. The results show that the extraction efficiency is sensitive to the extent to which the macrocycle cavity matches the metal ion size. Thus, while 3333–C12 is the best extractant for Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II) and Ag(I), 2323–C12 is a better extractant for Zn(II) and Cd(II) than is 4343–C12, while the reverse is observed for Pb(II). Another set of lipophilic hexamide and hexamine derivatives of azacrown[18]–N6 (Fig. 31) have been found to selectively extract Cu(II), Ag(I) and Hg(II) but not Cd(I) and some base metals [85]. A series of dihydroxycrownophanes (Fig. 32) show a high affinity toward Pb(II) even under acidic conditions, and excellent selectivity toward Ag(I) [84]. Recently two chromogenic and fluorogenic crown ether compounds have been prepared (Fig. 33) that can be used for the



trans

trans

trans

Fig. 28. Structures of thiacrown complexants.

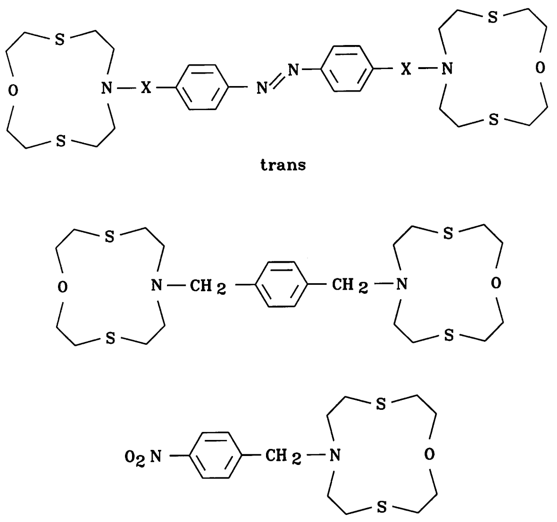


Fig. 29. Structures of photoresponsive thiacrown ethers.

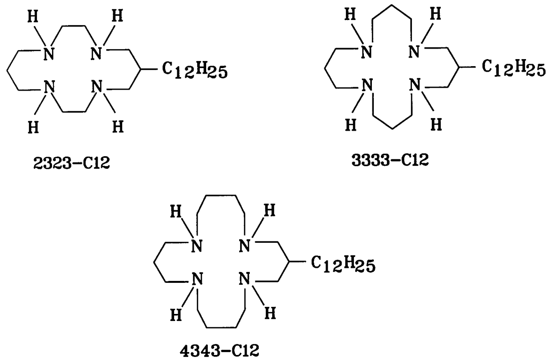


Fig. 30. Structures of the azacrowns 2323–C12, 3333–C12 and 4343–C12.

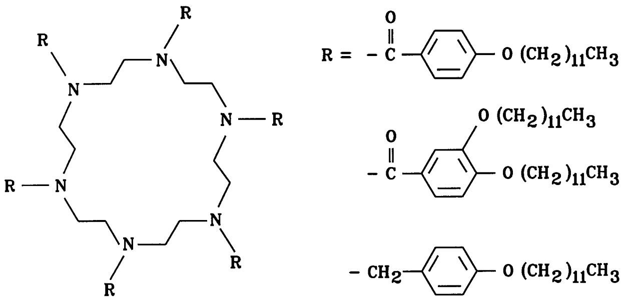


Fig. 31. Structures of substituted azacrowns.

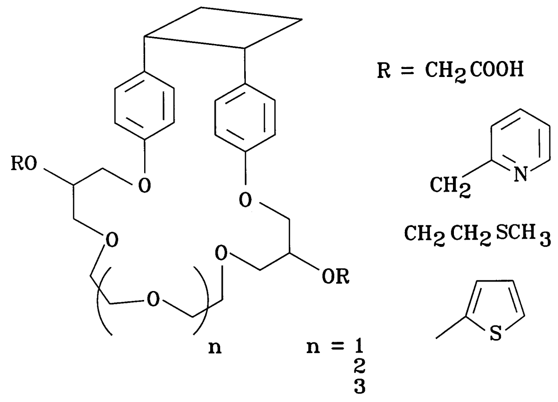
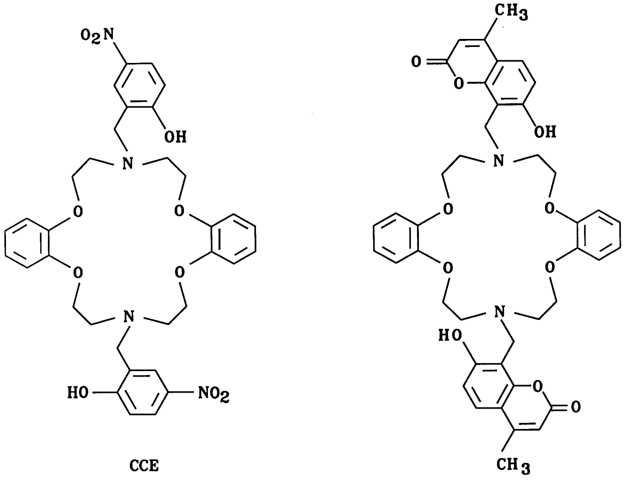


Fig. 32. Structures of crownophanes.



CCE

Fig. 33. Structures of chromogenic and fluorogenic crown ethers.

selective extraction and determination of heavy metal ions [88]. Each complexant exhibits a selectivity for Hg(II) that is greater than 10^6 over the next best extracted cation.

While macrocyclic compounds bearing only oxygen donor atoms are poor extractants for heavy and precious metal ions, they do, however, appear to be good extractants for oxophilic ions such as Ag(I), Tl(I) and Ba(II). A series of ring-contracted and ring-enlarged crown ethers have been reported, some of which selectively extract Ag(I), Tl(I) and Ba(II) in the presence of other alkali and alkaline earth metals (Figs. 34–36) [80–83]. Interestingly, the extractabilities of these macrocycles do not decrease monotonously with ring expansion.

There is a literature example of selenacrown ethers being used as extractants for heavy and precious metal ions. These compounds that are shown in Fig. 37 are good

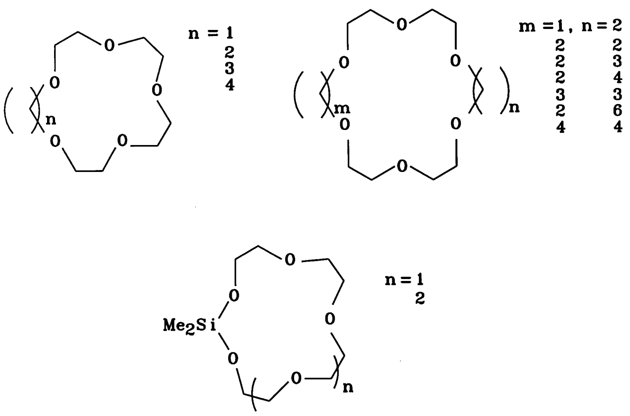


Fig. 34. Structures of crown ethers.

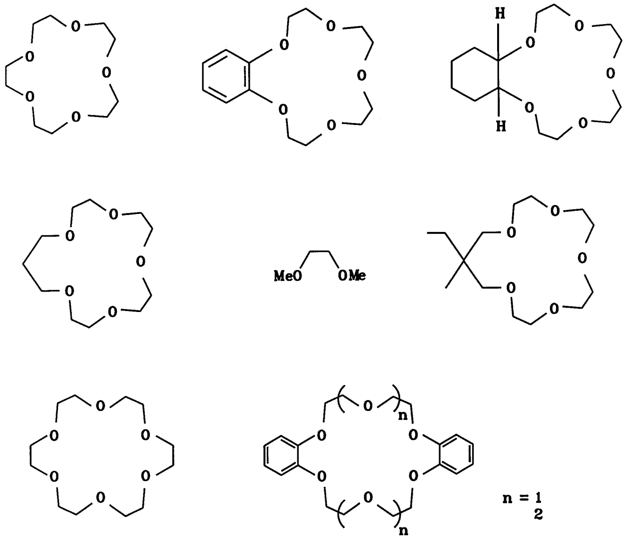
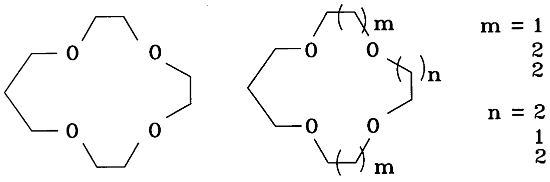


Fig. 35. Structures of crown ethers.

extractants for Cu(I), Pd(II), Hg(I) and MeHg(II) in the presence of Co(II), Ni(II) and Cu(I) [79]. Interestingly, the authors report that the extractabilities of those selenacrown ethers toward MeHg(II) ion are higher than those of the structurally corresponding thiacrown ethers. A study describes the use of thia and azacrown ethers (Fig. 38) for the separation of heavy metal ions in a neutral macrocycle-mediated emulsion liquid membrane system [110]. It is reported that Cu(II) is transported at higher rates than the other ions (Mn(II), Co(II), Ni(II), Zn(II), Sr(II), Cd(II) and Pb(II)) in the solution mixture. Others have chemically bonded the macrocycles T219C6 and T418C6 (Fig. 39) to silica gel and shown that they bind Cu(II), Fe(III) and other base metals less strongly than they do Pd(II), 13 to 16–Crown–4



benzo–12–crown–4

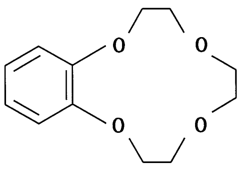
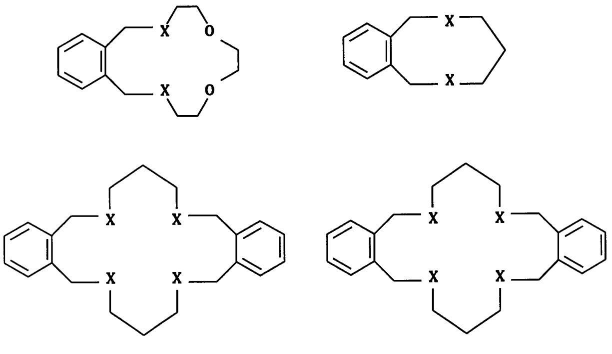


Fig. 36. Structures of crown ethers.

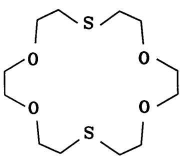


X = S, Se

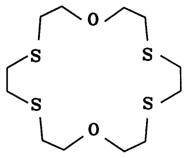
Fig. 37. Structures of thiacrown and selenocrown ethers.

Au(III), Ag(I) and Hg(II) [111]. Crown ethers containing an additional thiol group (Fig. 40) selectively extract Ag(I) and Hg(II) in the presence of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) [87]. Other thiacrown ethers that exhibit selectivity for Hg(II) and Ag(I) are shown in Fig. 41 [112], and another series of thiolariat ethers shown in Fig. 42 that exhibit a remarkable selectivity for Ag(I) and Pb(II) in the presence of other alkali and base metals [86]. A series of coronands containing 1,3,5-triazine thiols as redox switchable subunits can be used as extractants for Tl(I), Ag(I) and Hg(II), but the corresponding disulfides are poorer extractants for all three metal ions [113].

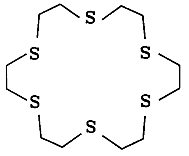
Molecular modeling studies on open-chain and cyclic thia compounds, along with



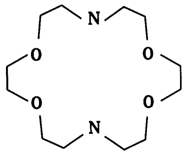
1, 4, 10, 13 – tetraoxa – 7, 16 –
dithiocyclooctadecane
(DT18C)



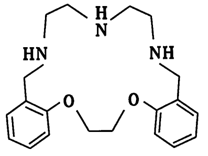
1,10 – dioxa – 4, 7, 13,16–
tetrathiocyclooctadecane
(TT18C6)



1, 4,7, 10,13, 16 –
hexathiacyclooctadecane
(HT18C6)

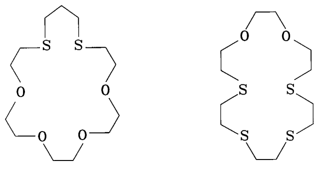


1,10 – diazo – 4, 7, 13,16–
tetraoxacyclohexadecane
(DA18C6)



1, 12,15 – triaza – 3, 4: 9,10 – dibenzo –
5, 8 –dioxycycloheptadecane
(DBN$_3$O$_2$)

Fig. 38. Structures of DT18C, TT18C6, HT18C6, DA18C6 and DBN3O2.



T$_2$ 19C6

T$_4$ 18C6

Fig. 39. Structures of T219C6 and T418C6.

their Ag(I) and Hg(II) complexes, show that the structures of the two sets of complexes are very similar with coordination occurring *via* three S donor atoms and the pyridine nitrogen. The higher extraction of Ag(I) is a consequence of the shorter bonding distances [114]. A series of tri- to hexa-dentate sulfur-containing macrocycles incorporating aromatic and heteroaromatic subunits are extractants for Ag(I), Hg(II), Au(III) and Pd(II). A trithiacrown with a benzo subunit preferentially extracts Ag(I) over Hg(II), and selectivity for Au(III) and Hg(II) over Pd(II) with the pyridine-substituted macrocycles shown in Fig. 43 is observed [115]. The

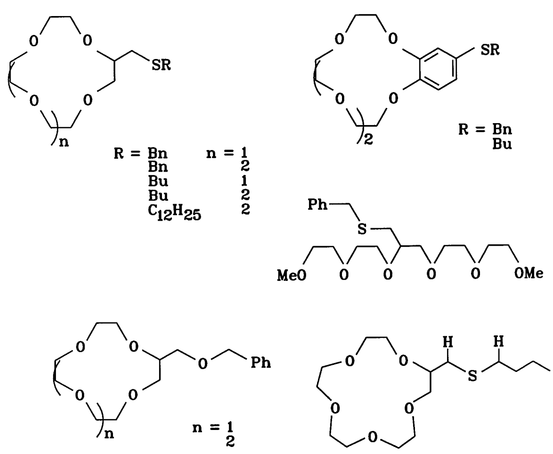


Fig. 40. Structures of sulfur derivatized crown ethers.

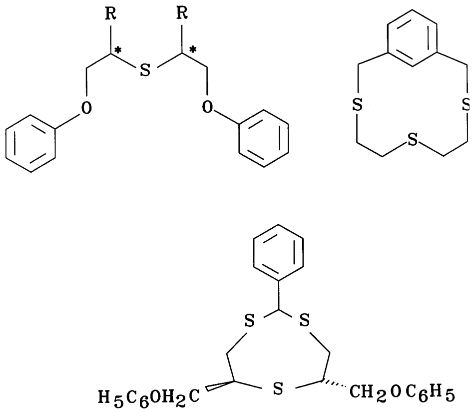
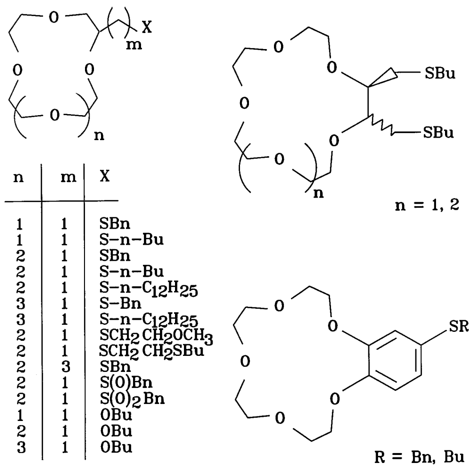


Fig. 41. Structures of thiacrown ethers.

extraction behavior of crown and related open-chain compounds with mixed O, S donor sets toward Ag(I) shows that a SOOS donor set is the most favorable for complex formation [116]. Bis-crown ethers having benzo-15-crown-5 units linked to 1,1-positions of Fe or Ru metallocenes have high affinities for Li(I), Na(I), K(I), Rb(I), Ag(I) and Tl(I) (Fig. 44). The extractability of metals using these bis-crown compounds is larger than that observed for the corresponding mono-crowns [117]. For the lipophilic monothia-15-crown-5, dithia-15-crown-5 and dithia-18-crown-6 compounds, and their oxygen analogs ($R = C_{12}H_{24}$) (Fig. 45), it has been found that the thia derivatives have a strong preference for Ag(I) extraction over alkali metal cations or Tl(I), but for the oxygen analogs the extraction of Ag(I) is low [91].



n	m	X
1	1	SBn
1	1	S-n-Bu
2	1	SBn
2	1	S-n-Bu
2	1	S-n-$C_{12}H_{25}$
3	1	S-Bn
3	1	S-n-$C_{12}H_{25}$
2	1	$SCH_2CH_2OCH_3$
2	1	SCH_2CH_2SBu
2	3	SBn
2	1	S(O)Bn
2	1	$S(O)_2Bn$
1	1	OBu
2	1	OBu
3	1	OBu

Fig. 42. Structures of thiolariat ethers.

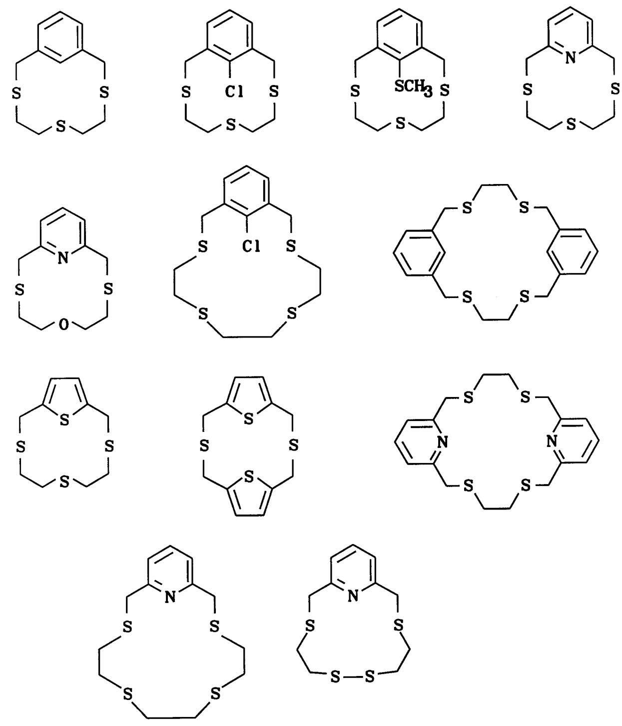


Fig. 43. Structures of thiacrowns.

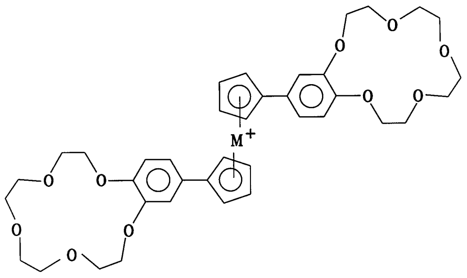
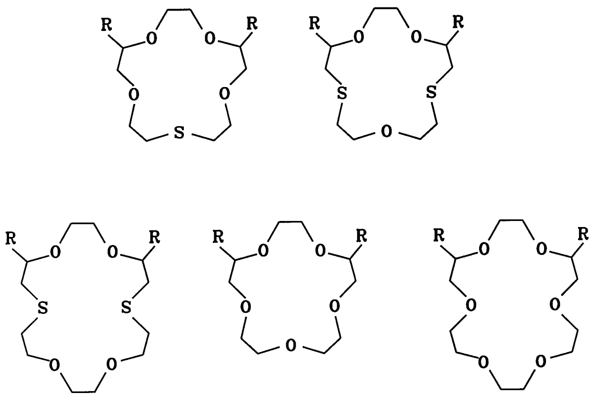


Fig. 44. Structure of metallocene-substituted crown ethers.



$(R=C_{12}H_{24})$

Fig. 45. Structures of crown and thiacrown ethers.

5.2. Limitations of chelate and crown complexants

It is clear that although there are several relatively inexpensive chelating agents available, and that some have found industrial applications, in many cases they are too unselective for general use. In addition to coordinating with heavy and precious metals they also bind appreciable amounts of alkali, alkaline earth and the lighter transition metals. This lack of selectivity decreases their efficiency and requires the subsequent separation of these metals after the extraction process. Crown ethers and cryptands, by contrast, show remarkable selectivity in their metal ion binding. Unfortunately, aside from some small scale analytical applications, it is problematic for them to be used as large scale extraction agents because of the following limitations [7]: (i) the preparation of crown ethers and cryptands almost always requires multiple-step synthetic procedures that give relatively low yields because of competing polymerization and other side reactions; (ii) typical synthetic procedures are performed under high-dilution conditions (10^{-4}M or less) in order to favor cyclization rather than intermolecular condensation. In industrial terms this translates into very large volumes of organic solvent being required for the preparation of relatively small quantities of the crown ether; (iii) some of the precursor materials are nitrogen and sulfur mustards, and are therefore extremely hazardous for use in large scale synthetic reactions.

5.3. Calixarenes

A recent development in the complexant field is the recognition that calixarenes may be useful extractants for metal ions, and to possibly make a contribution toward alleviating some of the problems associated with the application of the traditional crown ethers and cryptands for extraction purposes. This optimism results from calixarenes, like crowns, being preorganized complexants, yet, unlike crowns, they can be readily synthesized in large quantities. At present there are only a few examples in the literature of calixarenes being used as ligands for heavy and precious metals. One study reports that a series of Schiff base *p-tert*-butylcalix[4]arenes (Fig. 46) are good extractants for Cu(II) and Pb(II) [90]. However, most of the other alkali, alkaline earth and first row transition metals are also extracted in significant amounts by these derivatives. Another set of calixarene-based ligands (Fig. 47) have either ketone, thiocarbamoyl or thioether groups appended [118]. These complexants have been found to extract Ag(I) and Pb(II), with Na(I) and K(I) being extracted in smaller amounts. Another new class of derivatized calix[4]arenes bearing thiolate and *N*,*N*-dimethyldithiocarbamoyl functionalities on the lower rim have been synthesized (Fig. 48). The calix[4]arene with the thiolate functionalities is unselective and extracts all heavy and precious metals. By contrast the calix[4]arene with *N*,*N*-dimethyldithiocarbamoyl groups extracts Hg(II), MeHg(II), Ag(I), Pd(II) and Au(III), but not Pb(II), Cd(II), Ni(II) or Pt(II) [119]. Under photolytic conditions with a mixture of Pt(II) and Pt(IV), platinum extraction is also observed [120]. Since the extraction selectivities of these substituted

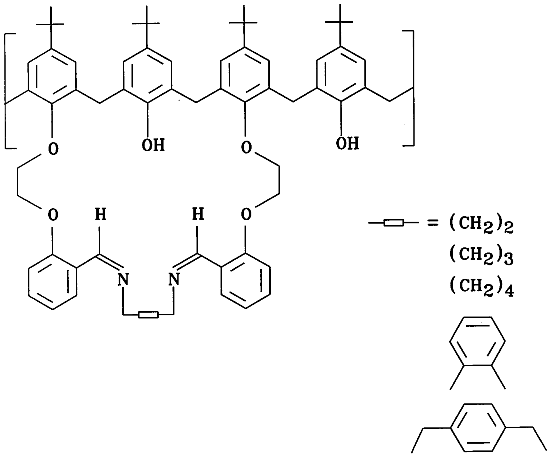


Fig. 46. Structure of Schiff base calix[4]arenes.

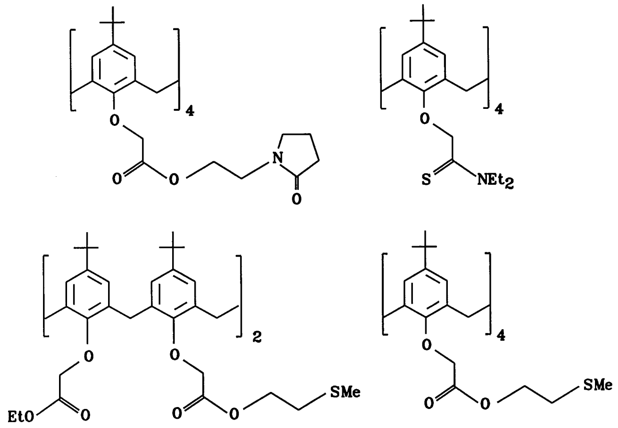


Fig. 47. Structures of derivatized calix[4]arenes.

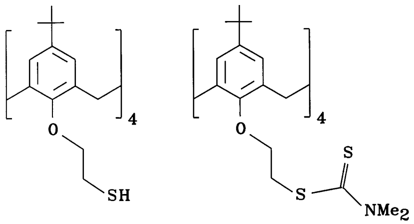


Fig. 48. Thiol and dithiocarbamoyl derivatized calix[4]arenes.

calix[4]arenes depend on whether there are hydrogen or *tert*-butyl groups on the upper rim it has been suggested that the size and shape of the calix[4]arene cavity may affect selectivity [121]. These preorganized ligands can be compared to crowns and thiacrowns [122]. A calix[4]arene with a diphenylphosphino group (Fig. 49) appended to the upper rim has been used as an extractant for heavy metals. The extractability for metal ions with this compound follows the sequence Hg(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II) > Al(III) > Na(I) > K(I). Since this sequence differs from that observed for triphenylphosphine it has been suggested that the cavity size of the calix[4]arene may be influencing the selectivity [123].

A family of calix[4]arenes having hydroxamate groups as metal binding sites and

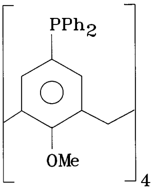


Fig. 49. Diphenylphosphino substituted calix[4]arene.

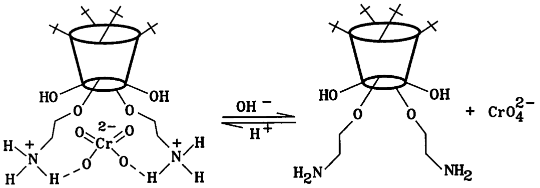


Fig. 50. Proton-switchable calix[4]arene extractant for Cr(VI).

either phenol or amide groups as hydrogen donors are extractants for nickel and copper. The calix[4]arenes that have phenolic groups extract Ni(II) in preference to Cu(II), while those lacking such H-donors extract Cu(II) in preference to both Ni(II) and Co(II) [92]. A calix[4]arene having alkylammonium substituents on the lower rim (Fig. 50) has been used as a "proton-switchable" extractant for chromate and dichromate anions [124].

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